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High-Resolution Solenoid Coil Nuclear Magnetic Resonance Probe for Superconducting Magnet Spectrometers

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16. ABSTRACT

A broadband probe having a tuning range of 20 to 65 MHz has been designed and built specifically to give maximum sensitivity per unit volume of sample. This is accomplished through use of a solenoid rf coil instead of the usual Helmholtz coil found in commercial probes for superconducting magnet systems. Improvement in signal-to-noise ratios approaches a factor of 3. Probe design considerations and construction materials are described.

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A broadband probe having a tuning range of 20 to 65 MHz has been designed and built specifically to give maximum sensitivity per unit volume of sample. This is accomplished through use of a solenoid rf coil instead of the usual Helmholtz coil found in commercial probes for superconducting magnet systems. Improvement in signal-to-noise ratios approaches a factor of 3. Probe design considerations and construction materials are described.

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INTRODUCTION

In the past decade the search for ever increasing sensitivity in multinuclei NMR experiments has taken several forms. Two prominent areas have been increasing sample size and increasing spectrometer magnetic field strength. While significant improvements have been achieved, results from these methods have fallen short of initial expectations.

Under certain conditions the signal-to-noise ratio (S/N) is proportional to the sample volume within the receiver coil. Increasing the sample size is a valid method of improving the S/N; however, the signal-to-noise ratio *per milliliter* usually drops as sample volume goes up. This is due in part to a smaller effective filling factor, since the magnetic flux lines do not extend through the center of the sample. Also, sensitivity is not optimized by increasing coil volume for samples which have limited availability (either because of expense or difficulty of preparation) where use of large volume rf coils and sample tubes is precluded.

It has long been thought that the S/N in an NMR experiment was proportional to the Larmor frequency raised to the three-halves power.[1] By simple reasoning, an increase in magnetic field strength of 2.1 T to 8.4 T (corresponding to proton resonance frequencies of 90 and 360 MHz, respectively) would result in an S/N improvement of eight (8). This theoretical improvement was never realized for the following reason. Of necessity, high-resolution NMR above 2.5 T requires the use of solenoid superconducting magnets. Samples are then aligned along the Z axis of the field, requiring a Helmholtz rf coil configuration, rather than the solenoid rf coil used in iron magnet systems. Recently, Hoult and Richards[2] have rederived the signal-to-noise ratio equation from first principles to evaluate coils of differing geometries. They have shown that the performance of a solenoid coil is approximately three times better than a Helmholtz coil with respect to S/N, due primarily to better penetration of flux lines into the sample. This factor of three greatly reduces the advantage expected in S/N for the spectrometers utilizing superconducting magnets. Solenoid-coil design probes have recently been developed for dedicated ^{13}C use[3] and for multinuclei spectroscopy.[4]

I. THE PROBE

The probe described here makes use of the solenoid coil geometry and is tunable over the range 20–65 MHz. This allows observation of nuclei ^{17}O through ^{31}P at a field of 3.5 T. Choice of a solenoid coil coupled with the requirement of orthogonality of the static magnetic field and the field generated by the coil requires spinning perpendicular to the Z magnetic axis. The probe design may be conveniently divided into a number of sections which will be discussed separately.

A. Spinning assembly

The design of the stator and rotor assembly was modified from a magic-angle spinner used in iron magnets.[5] There are several important criteria for materials for the spinner assembly. These materials must be (1) nonmagnetic; (2) rigid enough to maintain structural integrity; (3) machinable to a smooth surface; (4) inert to any chemicals which may come in contact with them; and (5) all materials must have compatible coefficients of thermal expansion. The probes should not contain materials having concentrations of nuclei which will be observed. Furthermore, protons should not be present to prevent possible heating problems from high powered decoupling.

The stator, Fig. 1, is constructed from a machinable glass, Macor,[6] chosen for its lack of protons, inertness to any but highly corrosive solvents, desirable thermal properties, and rigidity. The combination of these three requirements makes most machinable plastics unacceptable. Macor may be machined to close tolerances, giving a smooth surface on which gas bearings (A) may be

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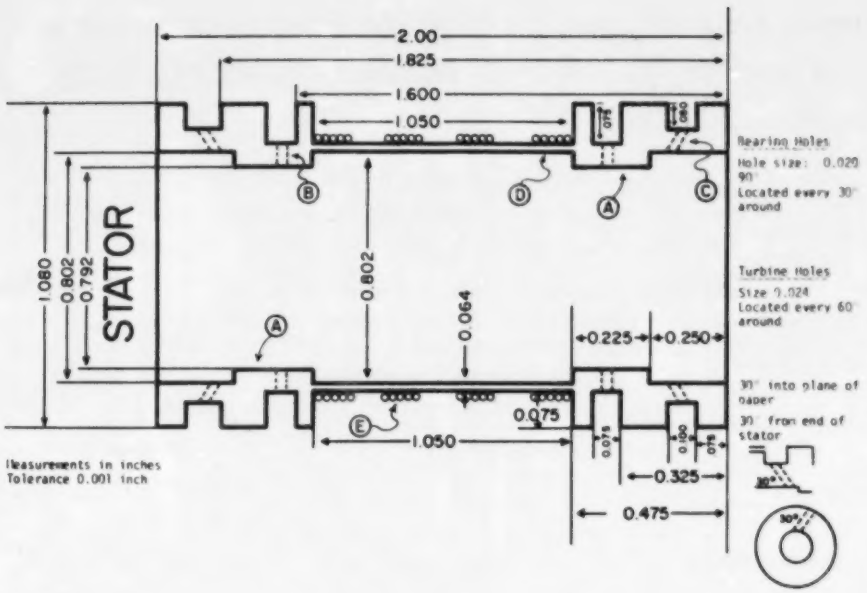

FIG. 1. Stator schematics, measurements in inches ±0.001 in. (A) bearing surface, (B) bearing gas jets, (C) turbine gas jets, (D) coil winding surface, and (E) observe coil.

formed at each end of the stator. These two bearings are created, when the sample cell is in place, using gas jets (B) placed at 30° intervals around the stator. The drive or turbine jets (C) which spin the sample are located just outside each bearing surface. The two drives are maintained at the same pressure and consist of six holes spaced 60° around the stator. Gas for the bearing and turbine jets is delivered through flexible tubing to a manifold at each end of the stator. Gas pressure for bearings and turbines may be varied independently by two in-line flow regulators to adjust the spin rate. The probe manifolds are constructed from a machinable plastic, Rulon.[7] End plates of Rulon keep the sample cell from falling out of the stator and provide exits for gas.

The sample cell (A), Fig. 2, is made from standard 20 mm Wilmad glass NMR tubes cut to length (37.48 mm), forming the second gas bearing surface. The edges are microfractured to present a smooth edge to O-ring seals to prevent cutting. End caps for these cells (B) serve to contain the sample and as rotors for the turbine gas jets. The caps are machined from Macor with provision for interchangeable O-ring seals. These O-rings (C) come in contact with the sample and care must be taken to choose the proper O-ring material, as individual O-ring materials swell in different solvents, potentially breaking the cells. We use several materials including viton, buna rubber, EPR, and nitrile depending on the solvent. O-rings are nominally $\frac{9}{16}$ in. i.d., $\frac{11}{16}$ in. o.d., and $\frac{1}{16}$ in. width. The standard cell holds 7.5 ml of sample which is loaded by a pipette or syringe through a threaded hole (D) in one end cap. This hole is sealed with a disposable nylon screw with an Allen type head.

It is interesting to note that the sample cell design lends itself to modification to form a spherical "microcell," Fig. 2, having a volume of 2.6 ml. This is very useful when a sample is available in very limited quantity. The microcell is formed from two Macor rotors having hemispherical cavities that form a sphere 17 mm in diameter when pushed together. This spherical cell eliminates concern over bulk magnetic susceptibility problems, and indeed, due to better sample utilization, gives a higher signal-to-noise ratio (relative to the full sized cell) than would be expected from the much smaller sample volume.

Rotors are equipped with flutes (E). These are not necessary for spinning, but may be useful in initiating spinning for heavier samples or ones which have become unbalanced. The spin stability does not seem to be affected at least to spin rates less than 250 Hz. The sample cells must be clean as spinning can be hindered by small amounts of oil or grease from fingers.

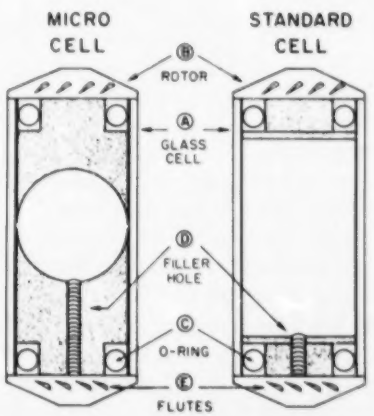

FIG. 2. Sample cell and rotor designs. In addition to these two cells, a third design used when there is no worry concerning a ^{13}C signal uses teflon in a vortex plug design using vanes to seal the opening, this prevents problems with O-ring swelling. Conical teflon rotors are screwed into the inserts to provide a drive surface.

FIG. 3. Decouple coil configuration.

B. Observe coil

The design of radiofrequency coils has been analyzed and discussed since the 1920's and very good reviews have been written recently.[2,8] The coil in our probe consists of four turns wound on the outside of the stator, Fig. 1 (E), giving an inside diameter of 0.93 in. and a length of 1.05 in. Each turn is composed of seven strands of 0.025 in. (22 AWG) silver-plated copper wire.[9] The loss in filling factor (~15%) from winding the coil on the outside of the stator rather than the inside was considered too small to offset the convenience of outside winding, at least during the development stage when many coils had to be wound. For smaller sample cells this loss becomes less acceptable, and we have wound coils on the inside of a form. The coil is wound on Delrin, a machinable plastic, while the two portions of the stator forming the turbine and bearing are of Macor. Unfortunately, in ^{13}C experiments, a plastic in the coil region gives rise to a broad hump in the spectrum and so cannot be used. The coil has a quality factor (Q) greater than 350, as measured at 50 MHz on a Hewlett–Packard vector impedance meter. Self-resonance limits the use of this coil to frequencies lower than 100 MHz. Two coil mounting methods were attempted. One involved use of cyanoacrylate glue applied as the coil was being wound. This technique provided easy mounting, but coils mounted in this fashion were seen to diminish in Q value over a period of a few months. This problem was not encountered using the second method where the coil was positioned after which three thin coats of Q dope were applied.

C. Decouple coil

The decouple coil, Fig. 3, is a one-turn Helmholtz design consisting of 0.025 in. diam. silver-plated copper wire, formed to lie as close to the sample as possible. Residual J couplings indicate that the decoupling field[10] extends approximately ±1.5 kHz, with 5 W of power.

D. Electronics

A lumped element design, Fig. 4, is used to provide broadband tuning and matching for the probe. The variable capacitors chosen should have certain characteristics to make them suitable for use in a broadbanded NMR probe. They must: (1) not be magnetic; (2) withstand the high voltages developed; (3) have sufficient range to cover frequencies of interest; (4) be stable once set; (5) be physically small; and (6) be externally adjustable for convenience. The capacitors used are all of the single turn air gap variety. These provide very rapid tuning from one frequency to another.[11] Capacitors are insulated from ground by mounting on plexiglass or Delrin support columns. The column lengths determine the position of each capacitor to minimize lead losses.

There is no separate channel provided for locking the spectrometer, but this is not necessary due to the high stability of superconducting magnets. Field homogeneity is optimized by tuning the observe coil to an abundant nucleus present in the sample (deuterium in our case), shimming and then tuning to the nucleus of interest.

E. Probe body

The shell is fabricated from standard aluminum tubing[12] in two sections. One covers the lower portion of the probe with the support tubes and remains secured most of the time. The second piece covers the electronics and spinner assembly and is easily removable to facilitate sample changes. The outside diameter of the tubing is machined to the proper size to fit in the magnet bore, in our case 73 mm with room temperature shims in place.

A drawing of the interior of the probe is given in Fig. 5. Aluminum tubes (A) serve as mechanical supports as well as paths for coaxial signal lines. Aluminum rods (B) are used to tune all capacitors. In order to avoid grounding problems, plexiglass or nylon sections are added to the rods where they pass through the aluminum base disk. A brass screwdriver shape head is mounted on top of each rod to fit the capacitor tuning slots.

The topmost plate, machined from teflon, provides a mount for the spinner assembly. Nylon screws anchor the spinner. The two remaining plates are of aluminum.

Double-sided glass epoxy printed circuit board (0.062 in.) serves in the electronics section to isolate each channel from the other and provide a common ground plane. In addition, these boards provide physical support for the teflon plate and spinner assembly.

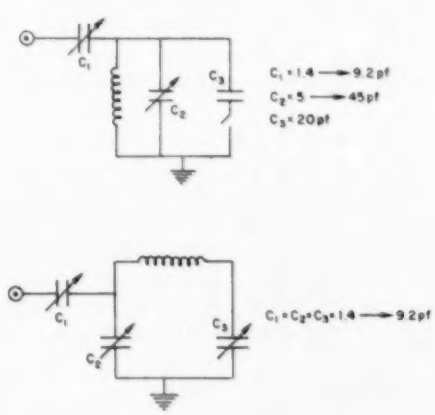

FIG. 4. Circuit diagram of the observe and decouple channels. Capacitance values are in picofarads.

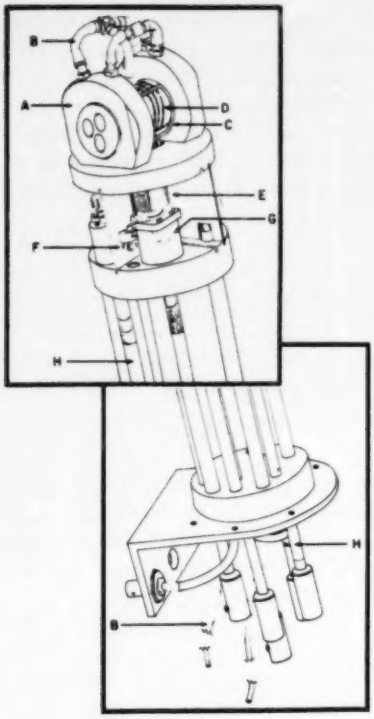

FIG. 5. Physical layout of probe: (A) manifold (Rulon), (B) gas inlet lines, (C) decouple coil, (D) observe coil, (E) tuning capacitor, (F) switch, (G) support column, and (H) control rods.

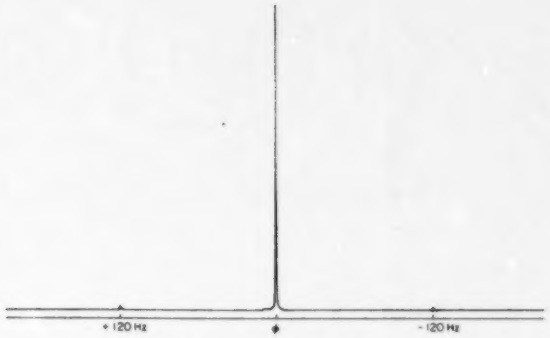

FIG. 6. Deuterium NMR spectrum of acetone-d_6 showing FWHH 0.25 Hz line, with less than 1% sidebands.

II. OPERATING CHARACTERISTICS

There was some concern during construction of this probe that the standard room temperature shims would not be able to shape properly the static magnetic field around the sample due to the unusual spinning axis, in the XY plane rather than along the Z axis. During the course of shimming, it was found that there were optimum orientations of the probe, which placed the axis of spinning along either the X or Y magnetic axis. After an initial learning period it is now possible to shim the magnet on a sample of acetone-d_6 from scratch in <15 min. to give an ^{2}H linewidth less than 0.5 Hz and with sidebands less than 1%, Fig. 6.

The probe may be tuned within seconds to the Larmor frequency of any nucleus within the range 20–65 MHz and matched to 50 Ω by use of control rods exterior to the probe, Fig. 6. The decouple channel may be tuned in an exactly analogous manner to minimize power reflectance.

Samples are generally spun at a rate between 80 and 150 Hz. Spinning rates above and below this range are possible but unnecessary. Spinning at this rate is fast enough to remove the problem of air bubbles in the sample. Bubbles, if present, form a clean, axial tube in the center of the cell which does not affect field homogeneity. Spinning is stable in this range, as samples have been spun for a period of days with little variation in spin rate.

III. PERFORMANCE

All spectra were obtained on the SEMINOLE spectrometer,[13] a synthesizer-based system with a Bruker 3.52 T superconducting magnet, operating in a quadrature detection Fourier transform mode. Pulse widths were in the range 25–50 μs for a 90° pulse at ≈150 W input power.

Results for ^{13}C and ^{89}Y spectra using the solenoid coil probe compared with results from conventional, in-house, probes employing Helmholtz coil geometries, show the expected S/N advantage, Table I. Compared with the best available commercial probes using Helmholtz design coils a factor of 2 increase in S/N per milliliter (corrected for field differences) is seen. Using matched filters and a 7.5-ml cell in each case, the ^{13}C spectrum of 90% dioxane (coupled) gives an S/N of greater than 500 : 1 rms, and 90% ethyl benzene gives a rms S/N of greater than 1500 : 1. The ^{31}P spectrum of 1% phosphoric acid has an S/N (rms) of more than 650 : 1. Ten percent trimethyl phosphite in the microcell using a 90° pulse of 30 μs and a matched filter of 1 Hz gives an S/N of 700 : 1 and 2400 : 1 coupled and decoupled, respectively.

This high sensitivity for low sample volume has made possible experiments which otherwise would be prohibited by time or cost. One important example of this is the natural abundance ^{13}C NMR study of double-stranded DNA which now includes preliminary spin–

TABLE I. Average probe sensitivities per unit volume.

Seminole probes[a]	Sample volume	^{13}C[b]	^{13}C[c]	^{13}C[d,f]	^{89}Y[e]
25 mm Helmholtz	20 ml	19	13	96	4
Solenoid full cell	7.5 ml	42	27	200	8
Solenoid microcell	2.6 ml	65	38	316	13

[a] All S/N given per milliliter of sample to compare sensitivity directly.
[b] 90% Dioxane, coupled, single 90° pulse, 2 Hz line broadening.
[c] ASTM standard, 60% benzene-d_6 in 40% p-dioxane, single 90° pulse, 1 Hz line broadening.
[d] 90% ethylbenzene, in 10% chloroform-d, decoupled, single 90° pulse, 2 Hz line broadening.
[e] Obtained on a low frequency version of the solenoid rf coil probe outlined in this paper, 3M $Y(NO3)_3$ in D_2O, single 90° pulse, 0.8 Hz line broadening.
[f] For reference, a typical commercial instrument using a Helmholtz coil for 20 mm sample tubes (the Bruker WP-200) gives an S/N for 10% ethylbenzene of 233 : 1. Corrected for magnetic field strengths, sample volume, and concentration, this becomes 105 : 1.

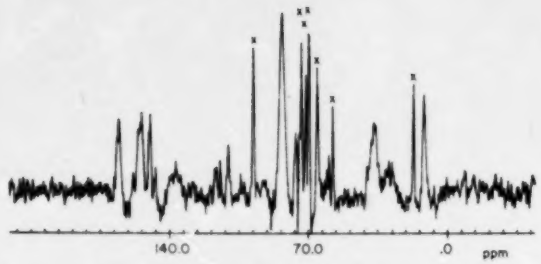

FIG. 7. Natural abundance ^{13}C spectrum of double stranded DNA. Obtained at 37.7 MHz, 90° pulse width 40 μs, 10,000 pulses over 15 h.

lattice relaxation time (T_1) data as well as chemical shifts and linewidths.[14] A sample spectrum is given in Fig. 7. The DNA spectra were obtained using the "microcell," which holds 2.6 ml of sample. Studies have shown that the microcell, which holds only 35% of the sample volume of the standard cell, gives an S/N between 50%–55% of the same concentration sample in the standard 7.5 ml cell. Therefore, the transverse spinning microcell provides the most efficient means of observation where limited sample quantities are concerned.

ACKNOWLEDGMENTS

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[1] A. Abragam, *The Principles of Nuclear Magnetism* (Clarendon, Oxford, 1961), pp. 82–83.
[2] D. I. Hoult and R. E. Richards, J. Magn. Reson. **34,** 71 (1976); for a given case a seven-fourths power field dependence is predicted.
[3] E. Oldfield and M. Meadows, J. Magn. Reson. **31,** 527 (1978).
[4] J. T. Bailey and G. C. Levy, 20th Experimental NMR Conference, Asilomar, California (1979).
[5] M. Alla and E. Lippma (private communication).
[6] Macor, Corning Glass Works, 80 Houghton Park, Corning, New York 14830.
[7] Rulon, Dixon Industries Corp., Metacom Avenue, Bristol, Rhode Island.
[8] J. Luznik and Z. Trontelj, J. Magn. Reson. **30,** 551 (1978).
[9] Silver-plated copper wire available, Magnet Wire, Inc., 11201 Northern Blvd., Corona, New York 11368.
[10] L. F. Johnson, *Topics in Carbon-13 NMR Spectroscopy,* Vol. 3, edited by G. C. Levy (Wiley-Interscience, New York, 1979), pp. 5–6.
[11] Suitable capacitors are available from several sources:
A. The MAC-series 1–15 pF, Cardwell Condensor Corp., 80 East Montauk Highway, Lindenhurst, Long Island, New York
B. 15–365 pF model, Etco Electronics ($0.35, #185VA), or Colectro Electronics ($3.10, #A1-283).
[12] Aluminum tubing, D6061T6, 3 in. o.d., 2¾ in. i.d., wall 0.125 in.
[13] The SEMINOLE Spectrometer is an in-house design broadband rf FT NMR instrument (Levy, G. C., Rosanske, R. C., Past, J.), 19th Experimental NMR Conference, Blacksburg, Virginia (1978).
[14] R. L. Rill, P. R. Hilliard, J. T. Bailey, and G. C. Levy, J. Am. Chem. Soc. **102,** 418 (1980).